

# **ATTRITION RESISTANT FISCHER-TROPSCH BASED ON FCC-SUPPORT**

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## **Abstract**

The Fischer-Tropsch (F-T) synthesis is the reaction of CO and H<sub>2</sub> (syngas) to produce a wide variety of hydrocarbons, oxygenates, and olefins. Iron or cobalt-based catalysts are used when the desired products are hydrocarbons. Because the reaction is highly exothermic, a slurry bubble column reactor (SBCR) is the reactor of choice. For coal-derived syngas, which typically has a H<sub>2</sub>/CO ratio of 0.5-0.7, iron-based catalysts are preferred over cobalt-based catalysts because (i) iron's high water gas shift (WGS) activity eliminates the need for an external shift step, and (ii) iron is significantly cheaper than cobalt.

Although F-T synthesis provides the best means currently available for conversion of coal to synthetic transportation fuels, there are two major barriers to its widespread commercialization: (i) severe attrition of iron catalysts in SBCRs, and (ii) a wide, non-selective product slate consisting of C<sub>1</sub> to C<sub>60</sub><sup>+</sup> hydrocarbons that must be extensively processed further to make fuels. Although the most

profitable Fischer-Tropsch product slate varies with location and other factors,  $C_{10}$  to  $C_{20}$  hydrocarbons are believed to be the products of choice in many cases, and offer an opportunity for Fischer-Tropsch products to be introduced in the market.

This project aims to develop an iron-based catalyst that addresses the two barriers that must be overcome for commercial success: (i) attrition resistance at the conditions found in a modern slurry reactor, and (ii) a selective product slate in the  $C_{10}$ - $C_{20}$  range. This novel concept is achieved by chain-limiting and attrition-resistant F-T catalysts for slurry reactors that maximize the production of  $C_{10}$ - $C_{20}$  hydrocarbons. The iron catalysts will be designed with multifunctional capability to oligomerize and hydrogenate lower olefins and hydrocrack the  $C_{20}^{+}$  hydrocarbons to produce the target  $C_{10}$ - $C_{20}$  hydrocarbons. The research will employ, among other measurements, attrition testing and F-T synthesis at high pressure. Catalyst activity and selectivity will be evaluated using a small fixed-bed reactor and a continuous stirred tank reactor.

#### A. SCOPE OF WORK

- The primary objective of this project is to develop novel attrition-resistant chain-limiting iron-based F-T catalysts for slurry reactors that maximize the production of high value  $C_{10}$ - $C_{20}$  hydrocarbons. This is a bench-scale project that will achieve the stated objective by conducting the FTS with a potassium and cerium (and possibly copper) promoted iron F-T catalyst deposited on an FCC support using novel sol gel and molten nitrate techniques;
- Using potassium to reduce the  $<C_{20}$  hydrocarbons, increase WGS activity, and increase the average molecular weight of the product;
- Using copper to facilitate iron oxide reduction, increase FTS activity, and increase the average molecular weight of product;
- Using potassium and cerium to decrease the heavy ends ( $>C_{20}$  fraction);
- Hydrogenating the oligomerized olefins using iron; operating FTS so as to get high chain growth probability; and
- Limiting the  $> C_{20}$  fraction by hydrocracking on the acidic support.

## B. TASKS TO BE PERFORMED

### **Task 1. Selection of FCC**

A number of fresh and spent FCC catalysts will be evaluated based on all available physical and chemical property data from the catalyst supplier and in-house NH<sub>3</sub> TPD, hydrogen chemisorption, and hydrogen TPR measurements.

### **Task 2. Catalyst Optimization**

Using the FCC catalyst supports selected in Task 1, promoted Fe catalysts will be prepared and evaluated by fixed-bed reactor testing for activity and C<sub>10</sub>-C<sub>20</sub> selectivity. The preparation techniques will include incipient wetness, sol-gel synthesis, and molten nitrate addition. Other variables evaluated will include levels of iron, potassium, cerium and copper. Each catalyst will be screened using H<sub>2</sub> chemisorption, H<sub>2</sub>/TPR and NH<sub>3</sub> TPD.

### **Task 3. Slurry Reactor Testing**

The two best catalysts determined in Task 2 will be evaluated in the slurry reactor in the temperature range of 250-300°C and at a pressure of 20 atm for 50-100 hours each. Based on these tests, an optimum catalyst (with respect to activity, long-term deactivation, C<sub>10</sub>-C<sub>20</sub> yield, and attrition resistance) will be determined.

### **Task 4. Catalyst Characterization**

The catalyst characterization methods to be used are discussed in detail in the methodology section of the proposal. This task will run throughout the project to provide catalyst characterization as needed to support the above three main tasks.